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**PATENT COOPERATION TREATY (PCT)
TRAITÉ DE COOPÉRATION EN MATIÈRE DE BREVETS (PCT)**

**CERTIFIED COPY OF THE INTERNATIONAL APPLICATION AS FILED
AND OF ANY CORRECTIONS THERETO**

**COPIE CERTIFIÉE CONFORME DE LA DEMANDE INTERNATIONALE, TELLE QU'ELLE
A ÉTÉ DÉPOSÉE, AINSI QUE DE TOUTES CORRECTIONS Y RELATIVES**

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Demande internationale n° }

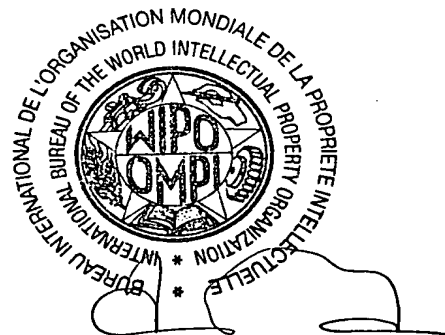
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19 September 2003
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World Intellectual Property Organization (WIPO)**

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Head, PCT Receiving Office Section
Chef de la section "office récepteur du PCT"

PCT REQUEST

5780-PCT

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0-1	International Application No.	PCT/IB 02 / 0 4 2 1 7
0-2	International Filing Date	14 OCTOBER 2002 (14.10.02)
0-3	Name of receiving Office and "PCT International Application"	INTERNATIONAL BUREAU OF WIPO PCT International Application
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0-4-1	Prepared using	PCT-EASY Version 2.92 (updated 01.06.2002)
0-5	Petition The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
0-6	Receiving Office (specified by the applicant)	International Bureau of the World Intellectual Property Organization (RO/IB)
0-7	Applicant's or agent's file reference	5780-PCT
I	Title of invention	SPIRO COMPOUNDS AS PERFUMING INGREDIENTS
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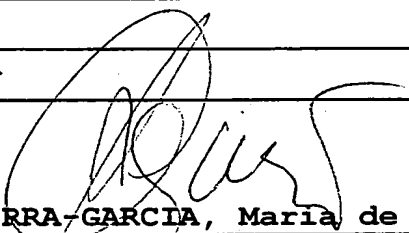
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V	Designation of States	
V-1	Regional Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	<p>AP: GH GM KE LS MW MZ SD SL SZ TZ UG ZM ZW and any other State which is a Contracting State of the Harare Protocol and of the PCT</p> <p>EA: AM AZ BY KG KZ MD RU TJ TM and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT</p> <p>EP: AT BE BG CH&LI CY CZ DE DK EE ES FI FR GB GR IE IT LU MC NL PT SE SK TR and any other State which is a Contracting State of the European Patent Convention and of the PCT</p> <p>OA: BF BJ CF CG CI CM GA GN GQ GW ML MR NE SN TD TG and any other State which is a member State of OAPI and a Contracting State of the PCT</p>
V-2	National Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	<p>AE AG AL AM AT AU AZ BA BB BG BR BY BZ CA CH&LI CN CO CR CU CZ DE DK DM DZ EC EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ OM PH PL PT RO RU SD SE SG SI SK SL TJ TM TN TR TT TZ UA UG US UZ VC VN YU ZA ZM ZW</p>
V-5	<p>Precautionary Designation Statement</p> <p>In addition to the designations made under items V-1, V-2 and V-3, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except any designation(s) of the State(s) indicated under item V-6 below. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit.</p>	
V-6	Exclusion(s) from precautionary designations	NONE
VI	Priority claim	NONE
VII-1	International Searching Authority Chosen	European Patent Office (EPO) (ISA/EP)

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VIII	Declarations	Number of declarations	
VIII-1	Declaration as to the identity of the inventor	-	
VIII-2	Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent	-	
VIII-3	Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application	-	
VIII-4	Declaration of inventorship (only for the purposes of the designation of the United States of America)	-	
VIII-5	Declaration as to non-prejudicial disclosures or exceptions to lack of novelty	-	
IX	Check list	number of sheets	electronic file(s) attached
IX-1	Request (including declaration sheets)	5	-
IX-2	Description	27	-
IX-3	Claims	4	-
IX-4	Abstract	1	EZABST00.TXT
IX-5	Drawings	0	-
IX-7	TOTAL	37	
	Accompanying items	paper document(s) attached	electronic file(s) attached
IX-8	Fee calculation sheet	✓	-
IX-17	PCT-EASY diskette	-	Diskette
IX-19	Figure of the drawings which should accompany the abstract		
IX-20	Language of filing of the international application	English	
X-1	Signature of applicant, agent or common representative		
X-1-1	Name (LAST, First)		
		SALVATERRA-GARCIA, Maria de Lurdes	

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10-2-2	Not received		
10-3	Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application		
10-4	Date of timely receipt of the required corrections under PCT Article 11(2)		
10-5	International Searching Authority	ISA/EP	
10-6	Transmittal of search copy delayed until search fee is paid		

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11-1	Date of receipt of the record copy by the International Bureau	
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SPIRO COMPOUNDS AS PERFUMING INGREDIENTS

Technical field

5 The present invention relates to the perfumery industry. It concerns more particularly an alcohol or ketone derivative having a spiro-type skeleton, and its use as perfuming ingredient. The invention also relates to the perfumed articles or perfuming compositions comprising, as active ingredient, an invention compound.

10 Prior art

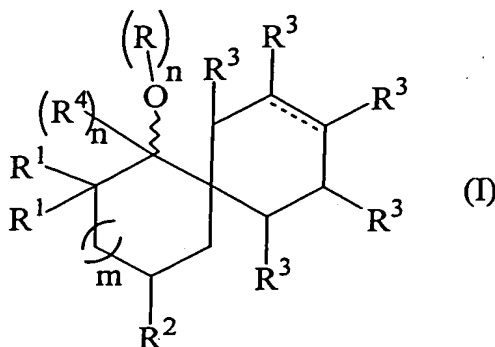
 Ketones and alcohol derivatives having a spiro-type skeleton are a quite known class of chemicals. However, and surprisingly, despite the large number of structures reported in the prior art, only few compounds of formula (I), hereinbelow described, are known.

15 For instance, Novikova *et al.* in their *Naftekhimiya*, **1994**, 24, 475 paper disclose, as chemical intermediates, the ketones 2,8-dimethyl spiro[5,5]undec-8-en-1-one and 2,9-dimethyl spiro[5,5]undec-8-en-1-one as well as the tertiary alcohols 1,9-dimethyl spiro[5,5]undec-8-en-1-ol and 1,8-dimethyl spiro[5,5]undec-8-en-1-one. Furthermore, Nakamura *et al.* in *Chem. Commun*, **2002**, 1648 disclose, as chemical compounds, the two
20 spiro-ketones 8,9-dimethyl spiro[5,5]undec-8-en-1-one and 7,8-dimethyl spiro[4,5]dec-7-en-1-one. However, in any of said documents mentioned hereinabove, there is no mention or suggestion of the specific organoleptic properties of the invention compounds, or of any potential use of said compounds as perfuming or flavoring ingredients.

 Between the compounds having a structure similar to those of the present
25 invention, only few are known in the prior art to have an odor which may be of interest for the perfumery industry. In US 4,668,432 are reported some alkyl substituted oxo-spiro[4,5]dec-7-ene derivatives which possess odors dominated by minty or animalistic top-notes. Similarly, US 4,622,172 discloses 9-methyl-11-isopropyl-spiro[5,5]undec-8-ene which imparts to compositions a fresh minty and spicy aroma. All the compounds
30 disclosed in US 4,668,432 and US 4,622,172 have a structure, and an odor, which differs from those of the present invention.

Description of the invention

We have now surprisingly been able to establish that a compound of formula (I)



wherein the index m is 0 or 1;

the symbol R represents a hydrogen atom, or a methyl or acetyl group;

the symbols R^1 , R^2 and R^4 represent a hydrogen atom or a methyl group;

10 the symbol R^3 represents a hydrogen atom, or a methyl or ethyl group; and two, three or four symbols amongst R^1 to R^4 represent simultaneously a group containing at least a carbon atom; and

the wavy and dotted lines represent a double bond, in which case n represents 0;

or

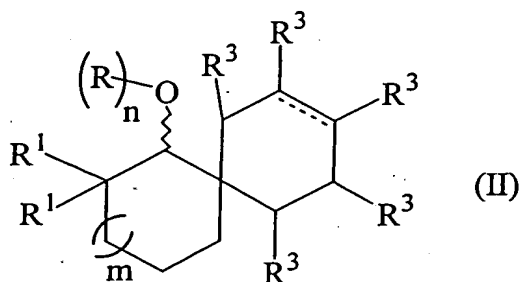
15 the wavy line represents a single bond, in which case the index n represents 1; and the dotted line represents a single or double bond;

possesses useful perfuming properties, of the woody and/or aromatic type, which render them very useful for the perfumery industry.

It is understood that, in a compound of formula (I), each of said group R^1 or R^3 20 may be identical or different to the other R^1 or R^3 groups, respectively. Moreover, the compound of formula (I) may be in the form of any one of its optical or regio isomers or of a mixture thereof. By "regio isomers" it is meant compounds which differ by the position wherein one or more R^3 symbols, not representing a hydrogen atom, are bonded to the spiro-skeleton. As non-limiting example of "regio isomers" one can cite 6,8,10-

trimethyl-spiro[4.5]dec-7-en-1-one and its regio isomer 7,9,10- trimethyl-spiro[4.5]dec-7-en-1-one.

A preferred embodiment of the invention is represented 'by' a compound of formula (II)



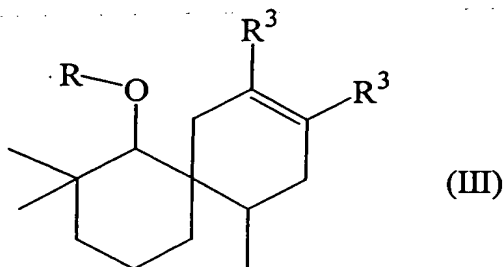
wherein the indexes m and n and the dotted and wavy lines have the same meaning as in formula (I);

the symbol R represents a hydrogen atom, or an acetyl group;

- 10 the symbols R¹ and R³ represent a hydrogen atom or a methyl group; and two, three or four symbols amongst R¹ and R³ represent simultaneously a methyl group ; and one, two or three of the R³ symbols, preferably non adjacent, represent simultaneously a methyl group.

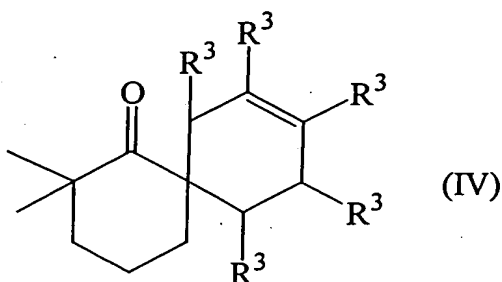
It is understood that, as for the compound of formula (I), each of said group R¹ or
15 R³ may be identical or different to the other R¹ or R³ group, respectively.

An even more preferred embodiment of the invention is represented by the alcohol derivative of the formula (III)



- 20 wherein the symbol R represents a hydrogen atom or an acetyl group; and
the symbols R³ represent, simultaneously, a hydrogen atom or
one symbol R³ represents a methyl group and the other symbol R³ represents a hydrogen atom.

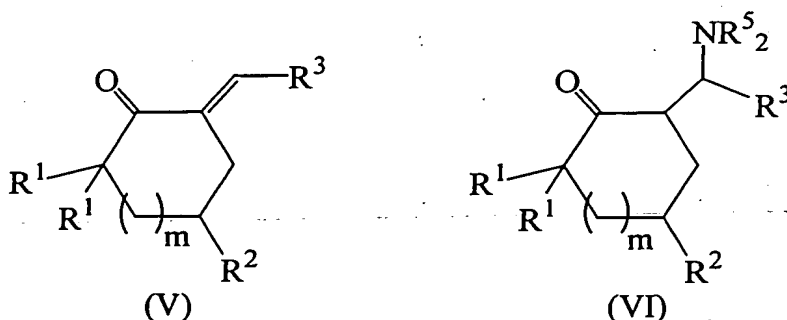
Alternatively, an equally more preferred embodiment of the invention is represented by the ketone of formula (IV)



wherein two, preferably non adjacent, symbols R^3 represent a methyl group and the other symbols R^3 represent a hydrogen atom.

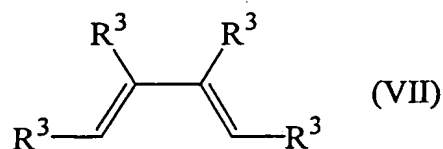
The compound of formulae (II) to (IV), as for those of formula (I), may be in the form of any one of its optical or regio isomers or of a mixture thereof.

The spiro compounds of formulae (I) to (IV) are susceptible of being obtained by a process involving a thermal, or Lewis acid, catalyzed Diels-Alder reaction between an enone of formula (V) or, alternatively, its equivalent Mannich base of formula (VI)



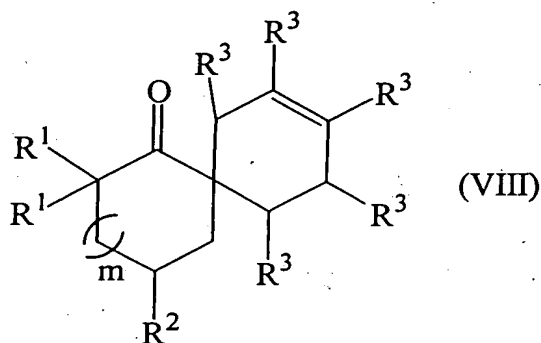
wherein the index m and the symbols R^1 , R^2 and R^3 have the same meaning as for formula (I) and the symbols R^5 represent, if taken independently, a methyl, ethyl, propyl or isopropyl group, or, if taken together, a saturated heterocycle such as morpholine, piperidine or pyrrolidine;

and a diene of formula (VII)



wherein the symbols R^3 have the same meaning as for formula (I),
to obtain a spiro-ketone (VIII)

5



wherein the index m and the symbols R^1 , R^2 and R^3 have the same meaning as in
formula (I).

10

Typical Lewis acid which can be used as catalysts are $AlCl_3$ or $BF_3 \cdot Et_2O$.

The reaction temperature of the Diels-Alder depends on the type of catalyst. In the
case of a thermal reaction, the temperature range is comprised between $100^\circ C$ and $240^\circ C$,
preferably between $140^\circ C$ and $200^\circ C$. In the case where a Lewis acid is used, the
temperature range is comprised between $-40^\circ C$ and $30^\circ C$, preferably between $-30^\circ C$ and
20°C.

15

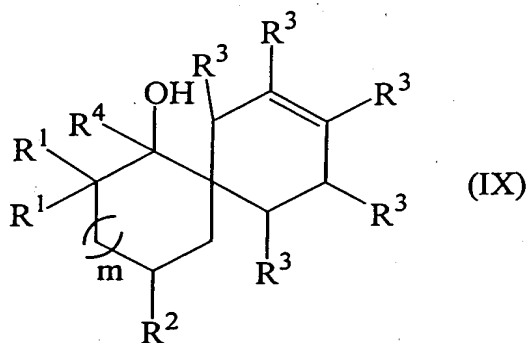
The Diels-Alder reaction may be performed in the absence or in the presence of a
solvent. When a solvent is required or used for practical reasons, then any current solvent
in Diels-Alder reactions can be used for the purposes of the invention provided it is
compatible with the starting and final products. Non-limiting examples include aromatic
solvents such as toluene or xylene, or alternatively, for acid catalyzed reactions it can be
used solvents such as CH_2Cl_2 , toluene or CH_3CN .

20

It will be also understood that whenever the diene (VII) is not a symmetric
compound, then the Diels-Alder reaction may lend to the formation of a spiro-ketone of

formula (VIII) in the form of a mixture of regio isomers. Additionally, as the compound of formula (VIII) possesses several chiral centers, the spiro-ketone of formula (VIII) may also be obtained in the form of a mixture of optical isomers. As well known by a person skilled in the art, the relative abundance between all the possible isomers obtained may depend on the nature of the starting compounds (VII) and (V) or (VI) as well as on the experimental conditions and possibly on the nature of the catalyst used.

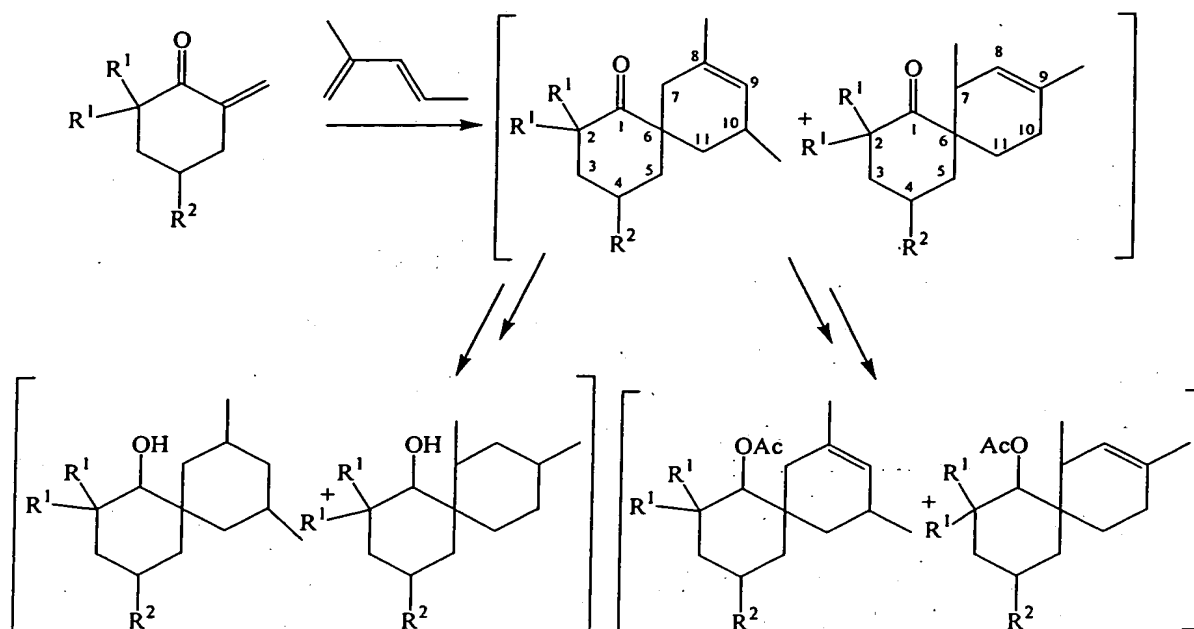
The spiro-ketone (VIII) thus obtained may subsequently be reduced, e.g using a hydride such as LiAlH_4 or an alkylating agent such as MeLi , to the corresponding spiro-alcohol of formula (IX)



wherein the index m and the symbols R^1 , R^2 , R^3 and R^4 have the same meaning as in formula (I).

If desired, using conventional methods well known to a person skilled in the art, the spiro-alcohol (IX) may subsequently be converted into an ester and/or the carbon carbon double bond reduced, e.g. by hydrogenation.

An example of the overall process is exemplified in scheme (1):



Scheme (1): Example of synthetic pathway to compounds of formula (I)

As previously mentioned, the compounds of formula (I) have odor properties which render them very useful for the perfumery industry. More precisely, the compounds of formula (I) display woody and/or aromatic fragrances, and are devoid of the minty or animalistic character typical of the prior art spiro-derivatives mentioned above. New compounds having such odor properties are highly desirable in the perfumery industry.

Examples of compounds of the formulae (I), (II), (III) or (IV) are various as will be shown below and in the examples.

An example is 2,2,9,11-tetramethylspiro[5.5]undec-8-en-1-yl acetate. Said compound has a very powerful woody odor with an excellent amber/ambergris connotation. The amber/ambergris notes, which are quite tenacious and strong, are well perceivable also as bottom notes. The overall odor is reminiscent of the Amberwood® (origin BASF AG) or 8,13:13,20-diepoxy-15,16-dinorlabdane (origin: Firmenich SA) odor. In addition to its excellent odor, 2,2,9,11-tetramethylspiro[5.5]undec-8-en-1-yl acetate seems to have also the advantage of not inducing anosmia as many other prior art compounds of the same olfactive family, e.g. Boisambrene® (origin: Henkel AG) or trans-1-(2,2,6-trimethyl-1-cyclohexyl)-3-hexanol (origin: Firmenich SA).

Another example of invention's compound belonging to the woody olfactive family is 2,2,11-trimethylspiro[5.5]undec-8-en-1-ol which has a excellent woody odor coming with camphor and earthy notes. The overall odor is characterized by a very appreciated and substantive, over a week, musky and woody-rooty undertone of the patchoulic-vetyver type, reminiscent of Tonalide® (origin: PFW, Holland). Thanks to its characteristic undertone, 2,2,11-trimethylspiro[5.5]undec-8-en-1-ol has the remarkable ability to confer richness, volume and persistence to a perfuming composition.

The saturated analogue of the previous compound, i.e. 2,2,11-trimethylspiro[5.5]undecan-1-ol, has an odor very similar, but drier, to that of 2,2,11-trimethylspiro[5.5]undec-8-en-1-ol.

A mixture of 2,2,7,9-tetramethylspiro[5.5]undec-8-en-1-one and its regio isomer 2,2,8,10-tetramethylspiro[5.5]undec-8-en-1-one possesses a quite complex odor profile but clearly belonging to the aromatic family. The fragrance of said mixture has aromatic, spicy, cardamom and terpenic notes, as well as camphor-woody under notes and a sulfury connotation, so that the whole scent reminds of the eucalyptus and clary-sage essential oils. Said mixture is well appreciated by perfumers for its very interesting aromatic note which is close to that of the noble laurel essential oil, an oil which can be used only in very limited amounts. Moreover, it has been found that the performance of said mixture in functional perfumery, e.g. softeners or detergents, are remarkable when compared to other products of the same olfactive family.

The lower analogues of the above-mentioned mixtures, e.g. having only three or two methyl substituents, have odors which tend to have different aromatic notes, as well as to be more camphoraceous and more volatile of the previous one. For instance a mixture of 2,2,10-trimethylspiro[5.5]undec-8-en-1-one and 2,2,7-trimethylspiro[5.5]undec-8-en-1-one has a pleasant and natural fragrance which is more camphor, woody, juniper and lavender than its tetramethyl analogue mentioned above, while 2,2-dimethylspiro[5.5]undec-8-en-1-one possesses an odor which is more terpeny, camphor, earthy and slightly tagetes than its tetramethyl analogue mentioned above.

The use of the compounds of formula (I) as perfuming ingredients, as well as the perfuming composition or perfumed article comprising as a perfuming ingredient an invention compounds, are also an object of the present invention.

The compounds of formula (I) are thus suitable, as perfuming ingredients, for use in all the fields of modern perfumery such as fine perfumery or functional perfumery. Examples of the perfuming compositions or perfumed articles in which it is possible to use or incorporate the invention compounds are perfumes, colognes or after-shave lotions, as well as perfumed soaps, preparations for the shower or the bath, such as bath salts, mousses, oils, gels or other preparations, products such as body oils, body-care products, body deodorants and antiperspirants, hair care products such as shampoos, ambient air deodorants or cosmetic preparations.

Other examples of perfuming compositions or perfumed articles are liquid or solid detergents for textile treatment, fabric softeners, or also in detergent compositions or cleaning products for cleaning dishes or varied surfaces, for industrial or household use.

As mentioned above, the perfuming compositions or perfumed articles cited hereinabove are also an object of the present invention.

In the above-mentioned applications, e.g. the perfuming compositions or perfumed articles, the compounds of formula (I) can be used alone, mixed together or mixed with other perfuming ingredients, solvents or additives commonly used in perfumery. The nature and type of these co-ingredients do not warrant a more detailed description here, which in any case would not be exhaustive, the skilled person being able to select them on the basis of his general knowledge and according to the nature of the product to be perfumed and the desired olfactory effect. These perfuming ingredients belong to chemical classes as varied as alcohols, aldehydes, ketones, esters, ethers, acetates, nitriles, terpene hydrocarbons, nitrogenous or sulphurous heterocyclic compounds and essential oils of natural or synthetic origin. Many of these ingredients are in any case listed in reference texts such as the book by S. Arctander, Perfume and Flavor Chemicals, 1969, Montclair, New Jersey, USA, or its more recent versions, or in other works of a similar nature, as well as in the abundant patent literature in the art of perfumery.

The proportions in which the compounds according to the invention can be incorporated in the different products mentioned above vary in a broad range of values. The range of concentrations depends on the nature of invention compound used, on the nature of the product to be perfumed and on the olfactory effect sought, as well as on the nature of the co-ingredients in a given composition when the compounds of the invention

are used in admixture with perfuming co-ingredients, solvents or additives commonly used in the art.

For instance, concentrations from 0.01% to 5.0%, by weight of these compounds, can be typically used. Preferably, for the more intense invention compounds, typical
5 concentrations are from 0.1% to 0.3%, by weight of these compounds, while for the less intense ones it is preferred to use concentrations ranging from 0.5% to 2%, by weight of these compounds. All the above percentages being expressed with respect to the weight of the perfuming composition in which invention compounds are incorporated.

Lower concentrations than these can be used when these compounds are directly
10 applied for perfuming some of the consumer products mentioned above.

The invention will now be described in further details by way of the following examples, wherein the abbreviations have the usual meaning in the art, the temperatures are indicated in degrees centigrade ($^{\circ}\text{C}$); the NMR spectral data were recorded with a 360MHz machine in CDCl_3 , the chemical displacement δ are indicated in ppm with
15 respect to the TMS as standard, the coupling constant J are expressed in Hz and all the abbreviations have the usual meaning in the art.

Example 1

20 Synthesis of some compounds according to the invention

GC analysis were performed using an HP-INNOWax Polyethylene glycol column (30 m x 0.25 mm) or an DB-1 Methyl Siloxane column (10 m x 0.1 mm).

25 1. General procedure for the preparation of Mannich bases

The ketone (1 mol), paraformaldehyde (1 mol) and dimethylamine hydrochloride (1.031 mol) were stirred in isopropanol (50 ml). Concentrated aqueous HCl (0.6 g) was added and the reaction was heated at reflux for 30 min. After cooling to room
30 temperature, the solid that had formed was filtered off, washed with acetone and dried. This solid was dissolved in water (200 ml) and the solution obtained was made alkaline by adding 50 % aqueous NaOH and then extracted with ether. The combined organic

phases were washed with brine and dried over anhydrous Na_2SO_4 . Filtration and evaporation of solvents gave the final compound practically pure.

6-[(dimethylamino)methyl]-2,2-dimethylcyclohexanone

5 Was obtained from 2,2-dimethylcyclohexanone in 82% yield.

MS: 183 (M^+ , 3); 95 (9); 69 (6); 58 (100); 41 (6).

$^1\text{H-NMR}$: 1.05 (s, 3 H); 1.21 (s, 3 H); 1.27 (qd, $J_q = 12$ Hz, $J_d = 3.7$ Hz, 1 H); 1.55 (td, $J_t = 12$ Hz, $J_d = 3.7$ Hz, 1 H); 1.66-1.93 (m, 4 H); 2.20 (s, 6 H); 2.15-2.28 (m, 1 H); 2.63-2.76 (m, 2 H).

10

2-[(dimethylamino)methyl]-4-methylcyclohexanone

Was obtained from 4-methylcyclohexanone in 57% yield and in the form of a 97:3 mixture of cis/trans isomers.

MS: 169 (M^+ , 2); 58 (100).

15 $^1\text{H-NMR}$: 1.01 (d, $J = 7$, 3 H); 1.07 (m, 1 H); 1.32-1.44 (m, 2 H); 1.91-2.07 (m, 1 H); 2.18-2.30 (m, 2 H); 2.20 (s, 6 H); 2.31-2.56 (m, 3 H); 2.64 (dd, $J_1 = 5$ Hz, $J_2 = 13$ Hz, 1 H).

2. General procedure for the thermal Diels-Alder reaction

20

A diene (2.53 mol), a Mannich base (0.437 mol) and hydroquinone (1.4 g) in toluene (400 ml) were heated in a steel autoclave at 170° C (external temperature) for 23 hours. After cooling to room temperature, the reaction was washed with 5 % aqueous HCl and brine. The aqueous phases were extracted with cyclohexane. The combined organic
25 phases were dried over anhydrous Na_2SO_4 . The residue obtained after filtration and evaporation of solvents was purified by column chromatography on silicagel (eluent: cyclohexane/ethyl acetate 19:1) and then by bulb-to-bulb distillation.

2,2-Dimethyl spiro[5.5]undec-8-en-1-one

30 Was obtained in 44% yield using butadiene and 6-[(dimethylamino)methyl]-2,2-dimethylcyclohexanone.

B.p. = 100-105° C/ 0.11 mbar

MS: 192 (M⁺, 52); 177 (6); 149 (26); 135 (13); 120 (100); 107 (26); 94 (57); 79 (91); 67 (18); 55 (21); 41 (44).

¹H-NMR: 1.11 (s, 3 H); 1.13 (s, 3 H); 1.46-1.86 (m, 7 H); 1.92-2.06 (m, 4 H); 2.20-2.28 (m, 1 H); 5.55-5.67 (m, 2 H).

5

Mixture of 2,2,7,9-tetramethyl spiro[5.5]undec-8-en-1-one and 2,2,8,10-tetramethyl spiro[5.5]undec-8-en-1-one

Was obtained in 78% yield using 2-methyl-1,3-pentadiene and 6-[(dimethylamino)methyl]-2,2-dimethylcyclohexanone. GC shows a mixture of 4 isomers in the following ratio: 7/8/32/53

10

B.p. = 120-123°C/ 0.043 mbar.

MS (major isomer): 220 (M⁺, 55); 205 (15); 191 (6); 177 (18); 148 (12); 135 (12); 121 (44); 107 (49); 93 (33); 82 (100); 67 (32); 41 (44).

15

¹H-NMR: 0.74-0.97 (m, 3 H); 1.05-1.20 (m, 7 H); 1.30-2.00 (m, 11 H); 2.10-2.46 (m, 2 H); 5.05-5.24 (m, 1 H).

Mixture of 2,2,7-trimethyl spiro[5.5]undec-8-en-1-one and 2,2,10-trimethyl spiro[5.5]undec-8-en-1-one

Was obtained in 21% yield using 1,3-pentadiene and 6-[(dimethylamino)methyl]-2,2-dimethylcyclohexanone. GC shows a mixture of 4 isomers in the following ratio: 5/29/32/34.

20

Organoleptic properties: a pleasant and natural juniper, pine, woody and balsamic odor with linalool and lavender bottom notes.

B.p. = 52-63°C/ 0.18 mbar.

25

MS (major isomer): 206 (M⁺, 58); 191 (34); 163 (71); 147 (6); 134 (74); 121 (35); 108 (100); 93 (88); 82 (57); 67 (32); 55 (31); 41 (60).

¹H-NMR: 0.77-1.20 (m, 9 H); 1.33-2.48 (m, 11 H); 5.36-5.68 (m, 2 H).

30

Mixture of 4,7,9-trimethyl spiro[5.5]undec-8-en-1-one and 4,8,10-trimethyl spiro[5.5]undec-8-en-1-one

Was obtained in 32 % yield from 2-methyl-1,3-pentadiene and 2-[(dimethylamino) methyl]-4-methylcyclohexanone. GC shows a mixture of 5 stereoisomers in the following ratio: 4.5/5.5/12/20/58.

Organoleptic properties: nice multi-odored woody, vetiveryl acetate, rosy and lilac odor.

5 B.p. = 80° C/ 0.03 mbar.

MS (major isomer): 206 (M^+ , 53); 191 (17); 177 (18); 163 (35); 125 (18); 107 (19); 91 (22); 82 (100); 67 (28); 55 (11); 41 (13).

$^1\text{H-NMR}$: 0.74-1.20 (m, 7 H); 1.23-2.73 (m, 14 H); 5.13-5.28 (m, 1 H).

10 3. General procedure for the reduction of Diels-Alder adducts by an hydride

A solution of spiro-ketone (145.6 mmol) in THF (150 ml) was added to a cold (0° C) slurry of LiAlH_4 (5.7 g, 150 mmol) in THF (600 ml). The reaction was warmed up to room temperature, and then heated at 50° C for 4 hours. After cooling to 0° C, were
15 successively and cautiously added water (6 ml), 5 % aqueous NaOH (17 ml) and again water (6 ml). The reaction was stirred at room temperature until it became a white slurry. Said slurry was dried by adding anhydrous Na_2SO_4 . Filtration and evaporation of solvents was followed by bulb-to-bulb distillation.

20 *(5RS,6SR,10SR)-10-ethyl-6,8-dimethyl spiro[4.5]dec-7-en-1-ol*

Was obtained in 95 % yield from (5RS,6SR,10SR)-10-ethyl-6,8-dimethyl spiro[4.5]dec-7-en-1-one . GC shows a 9:1 ratio of diastereoisomers.

Organoleptic properties: woody, camphoreaceous, ginger odor

B.p. = 100-105° C / 0.36 bars.

25 MS: 208 (M^+ , 4); 190 (42); 175 (13); 161 (78); 148 (35); 133 (42); 125 (49); 119 (96); 105 (59); 91 (48); 82 (100); 67 (58); 55 (41); 41 (54).

$^1\text{H-NMR}$: 0.88-0.98 (m, 6 H); 1.05-1.10 (m, 1 H); 1.30-1.80 (m, 12 H); 1.85-2.00 (m, 2 H); 2.16-2.27 (m, 1 H); 3.91-3.97 (m, 1 H); 5.15-5.19 (m, 1 H).

30 *R-6-ethyl-T-10-methyl-spiro[4.5]decan-1-ol*

Was obtained in 88 % yield from R-6-ethyl-T-10-methyl-spiro[4.5]decan-1-one. Isomer ratio (by GC): 78/8/5.

Organoleptic properties: patchouli, borneol and camphoraceous odor

B.p. = 102°C / 1.7 mbar.

MS: 196 (M⁺, 17); 167 (18); 149 (100); 123 (63); 107 (20); 95 (60); 81 (54); 67 (47); 55 (59); 41 (68).

5 ¹H-NMR: 0.80-1.10 (m, 2 H); 0.89 (t, J = 7.1 Hz, 3 H); 0.98 (d, J = 7.1 Hz, 3 H); 1.29-1.84 (m, 13 H); 1.97-2.05 (m, 1 H); 3.87-3.94 (m, 1 H).

Mixture of 6,8-dimethyl-spiro[4.5]dec-7-en-1-ol and 7,9-dimethyl-spiro[4.5]dec-7-en-1-ol

Was obtained in 99 % yield from a mixture of 6,8-dimethyl-spiro[4.5]dec-7-en-1-one and
10 7,9-dimethyl-spiro[4.5]dec-7-en-1-one. GC shows a ratio of isomers of 10/21/63.

B.p. = 95°C / 0.12 mbar

MS (major isomer): 180 (M⁺, 6); 162 (77); 147 (87); 134 (86); 119 (50); 105 (98); 91 (90); 82 (100); 67 (100); 55 (48); 41 (91).

¹H-NMR: 0.86-1.15 (m, 3 H); 1.22-2.30 (m, 15 H); 3.65-3.99 (m, 1 H); 5.19-5.46 (m, 1
15 H).

4. General procedure for the esterification of spiro-alcohols

Acetyl chloride (215.4 mmol) was added slowly to a solution of alcohol (134.6 mmol),
20 pyridine (228.8 mmol) and dimethylaminopyridine (27 mmol) in dry CH₂Cl₂ (600 ml). After stirring for 5 hours at room temperature, the solvent was evaporated under *vacuo*. The residue was taken up in pentane and the mixture washed with water, aqueous saturated NaHCO₃, 10 % aqueous CuSO₄ and brine. The organic phase was dried over anhydrous Na₂SO₄. After filtration and evaporation of solvents, the residue was purified
25 by bulb-to-bulb distillation.

Alternatively the esterification may be carried according to the following procedure:

Acetic anhydride (12.22 mmol) was added to a solution of alcohol (6.11 mmol), pyridine (13.44 mmol) and dimethylaminopyridine (0.61 mmol) in CH₂Cl₂ (15 ml). The reaction was stirred for 4 hours at room temperature, then concentrated under *vacuo*. The residue
30 was purified by bulb-to-bulb distillation.

R-6-ethyl-T-10-methyl-spiro[4.5]dec-1-yl acetate

Was obtained in 62% yield from R-6-ethyl-T-10-methyl-spiro[4.5]decan-1-one.

Organoleptic properties: a very elegant woody, caryophyllene, vetiveryl acetate and slightly sandalwood odor with amber and camphoraceous under notes

5 B.p. = 70° C / 0.15 mbar

MS: 238 (M⁺, 1); 209 (4); 178 (16); 163 (13); 149 (100); 135 (8); 123 (21); 107 (17); 95 (29); 81 (28); 67 (25); 43 (67); 41 (29).

¹H-NMR: 0.87 (d, J = 6.7 Hz, 3 H); 0.91 (t, J = 7.3 Hz, 3 H); 0.97-1.10 (m, 2 H); 1.30-1.80 (m, 13 H); 2.04 (s, 3 H); 2.13-2.20 (m, 1 H); 4.88 (t, J = 7.3 Hz, 1 H).

10

Mixture of 6,8-dimethyl-spiro[4.5]dec-7-en-1-yl acetate and 7,9-dimethyl-spiro[4.5]dec-7-en-1-yl acetate

Was obtained in 99% yield from a mixture of 6,8-dimethyl-spiro[4.5]dec-7-en-1-ol and 7,9-dimethyl-spiro[4.5]dec-7-en-1-ol. The GC ratio of isomers was 13/8/75.

15 B.p. = 70 °C/0.06 mbar.

MS (major isomer): 222 (M⁺, 1); 180 (5); 162 (48); 147 (53); 134 (70); 119 (37); 105 (43); 91 (37); 82 (53); 67 (43); 43 (100); 41 (36).

¹H-NMR: 0.82-1.20 (m, 3 H); 1.32-2.27 (m, 19 H).

20 *(5RS,6SR,10SR)-10-ethyl-6,8-dimethylspiro[4.5]dec-7-en-1-yl acetate*

Was obtained in 97% yield from (5RS,6SR,10SR)-10-ethyl-6,8-dimethyl spiro[4.5]dec-7-en-1-ol. GC shows a 4.5/85.1/8.4 ratio of isomers.

Organoleptic properties: a fairly strong woody, vetiveryl acetate sesquiterpenes, odor.

B.p. = 78-83° C / 0.078 mbar.

25 MS: 250 (M⁺, 1); 190 (72); 175 (25); 161 (100); 148 (55); 134 (37); 126 (24); 119 (43); 108 (29); 93 (28); 82 (41); 67 (19); 43 (12).

¹H-NMR: 0.89 (d, J = 7.5 Hz, 3 H); 0.94 (t, J = 7.3 Hz, 3 H); 0.97-1.15 (m, 1 H); 1.38-1.45 (m, 1 H); 1.51-1.81 (m, 8 H); 1.61 (broad s, 3 H); 1.91-2.11 (m, 2 H); 2.03 (s, 3 H); 4.87 (t, J = 6 Hz, 1 H); 5.14-5.17 (m, 1 H).

5. General procedure for the alkylation of Diels-Alder adducts by MeLi

A solution of spiro-ketone (43 mmol) in dry diethylether (30 ml) was added to a solution of MeLi in dry diethylether (1.6 M, 40 ml, 64 mmol) at -78°C . The reaction was warmed up to room temperature and stirred overnight. After cooling at 0°C , water was added and the mixture was extracted with ether. The combined organic phases were washed with brine and dried over solid Na_2SO_4 . After filtration and evaporation of solvents, the product was purified by column chromatography over silicagel (eluent = cyclohexane/ethyl acetate 29:1) and bulb-to-bulb distillation.

Mixture of 1,6,8-trimethyl-spiro[4.5]dec-7-en-1-ol and 1,7,9-trimethyl-spiro[4.5]dec-7-en-1-ol

Was obtained in 40 % yield from a mixture of 6,8-dimethyl-spiro[4.5]dec-7-en-1-one and 7,9-dimethyl-spiro[4.5]dec-7-en-1-one. The GC ratio of isomers was 4/4/4/5/6/74.

Organoleptic properties: borneol, camphoraceous and patchouli odor.

B.p. = 68°C / 0.04 mbar

MS (major isomer): 194 (M^+ , 7); 176 (29); 161 (28); 147 (11); 136 (46); 121 (40); 119 (40); 107 (38), 105 (39); 93 (40); 91 (41); 82 (58); 67 (43); 55 (20); 43 (100).

$^1\text{H-NMR}$: 1.07 (d, $J = 7.1$ Hz, 3 H); 1.27 (s, 3 H); 1.35-2.13 (m, 12 H); 1.61 (s, 3 H); 5.34-5.38 (m, 1 H).

Example 2

Synthesis of some compounds according to the invention

Ethylidene-dimethylcyclohexanone was obtained according to J.T.A. Reuvers, A. de Groot, Synthesis 1982, 1105 in the form of a mixture of E/Z isomers (87/13).

1. General procedure for the thermal Diels-Alder reactions

A mixture of 5g (32.8 mmol) ethylidene-dimethylcyclohexanone and 3 equivalents of diene was heated in an autoclave for 18h at 200°C . After cooling and elimination of

polymers by bulb to bulb distillation, the spiro-ketones were purified by flash chromatography, (pentane/ether = 99/1) and bulb to bulb distillation.

2,2,11-trimethylspiro[5.5]undec-8-en-1-one

- 5 Was obtained from ethylidene-dimethylcyclohexanone and butadiene in 51% yield and in the form of a mixture of 2 isomers in the following ratio: 13/1.

Organoleptic properties: camphoraceous.

MS : 206(M⁺, 68) ; 134 (75), 93 (100), 79 (83), 41 (91).

- ¹H-NMR (main isomer) : 0.73 (d : J = 7, 3H), 1.08 (s, 3H), 1.10 (s, 3H), 1.50-1.85 (m, 7H), 1.97 (m, 2H), 2.22 (m, 1H), 2.33 (sept. : J = 7, 1H), 5.51 (m, 1H), 5.65 (m, 1H).
- 10

2,2,9,11-tetramethylspiro[5.5]undec-8-en-1-one

- Was obtained from ethylidene-dimethylcyclohexanone and isoprene in 90% yield and in the form of a mixture of 2 isomers in the following ratio: 2/3. The two stereoisomers may be separated by preparative GC on a Supelcowax-10 column, 30m x 0.53mm, film 2μ.
- 15

Organoleptic properties: a very natural aromatic, green and fruity odour with artemisia and ginger bottom notes.

minor isomer:

- MS : 220(M⁺48), 192(43), 135(48), 122(65), 107(100), 93(59), 79 (38), 67(31), 55(42), 41(78).
- 20

¹H-NMR (C₆D₆): 0.74 (d : J = 7, 3H), 1.01 (s, 3H), 1.12 (s, 3H), 1.30-1.85 (m, 8H), 1.53 (large s, 3H), 1.96 (d : J = 16, 1H), 2.09 (d : J = 16, 1H), 2.52 (sept. : J = 7, 1H), 5.32 (m, 1H).

major isomer:

- MS : 220(M⁺67), 148(29), 121(51), 107(100), 93(61), 82(69), 67(35), 55(43), 41(82).
- ¹H-NMR (C₆D₆): 0.75 (d : J = 7, 3H), 0.99 (s, 3H), 1.12 (s, 3H), 1.25-1.75 (m, 8H), 1.56 (large s, 3H), 2.07 (m, 2H), 2.57 (sept. : J = 7, 1H), 5.13 (m, 1H).
- 25

2,2,7,11-tetramethylspiro[5.5]undec-8-en-1-one

- 30 Was obtained from ethylidene-dimethylcyclohexanone and piperylene in 32% yield and in the form of a mixture of 2 isomers in the following ratio: 1/1. The two stereoisomers

may be separated by preparative GC on a Supelcowax-10 column, 30m x 0.53mm, film 2 μ .

Organoleptic properties: a woody, pine and aromatic odor.

- 1st eluted peak:

5 MS : 220(M⁺, 98) ; 153(93), 107(100), 93(64), 68(26), 55(18), 41(22).

¹H-NMR : 0.73 (d : J = 7, 3H), 0.79 (d : J = 7, 3H), 1.06 (s, 3H), 1.11 (s, 3H), 1.50-1.98 (m, 8H), 2.33 (sept. : J = 7, 1H), 2.44 (m, 1H), 5.53 (m, 2H).

- 2nd eluted peak :

MS : 220 (M⁺, 50) ; 205(100), 148(46), 121(35), 107(80), 93(42), 82(48), 69(16), 42(23).

10 ¹H-NMR : 0.77 (d : J = 7, 3H), 0.90 (d : J = 7, 3H), 1.13 (s, 6H), 1.41-1.98 (m, 8H), 2.07 (sept. : J = 7, 1H), 2.73 (m, 1H), 5.29 (m, 1H), 5.60 (m, 1H).

The same reaction, performed in toluene at -20° in the presence of 1eq. of AlCl₃ gave the same mixture of isomers but in a ratio of 7:1 in 75% yield after distillation.

15 2. General procedure for the hydrogenation of spiroketones

A mixture of the spiro-ketone (0.1 mole) in 200 ml of EtOH was hydrogenated at 20° and atmospheric pressure in the presence of 100mg of 5% Pd/C. When 1 equivalent of H₂ was absorbed, the mixture was filtered on Celite, concentrated under vacuum and purified by bulb to bulb distillation.

20

2,2,7-trimethylspiro[5.5]undecan-1-one

Was obtained from 2,2,11-trimethylspiro[5.5]undec-8-en-1-one in quantitative yield and in the form of a mixture of 2 isomers in the following ratio: 13/1.

MS (main isomer) : 208 (M⁺, 62) ; 136(42), 126(94), 109(56), 95(92), 81(92), 67(75),

25

55(71), 41(100).

¹H-NMR (main isomer) : 0.66 (d : J = 7, 3H), 1.06 (s, 3H), 1.10 (s, 3H), 1.14-1.92, (m, 14H), 2.19 (m, 1H).

2,2,7,9-tetramethylspiro[5.5]undecan-1-one

30 Was obtained from 2,2,9,11-tetramethylspiro[5.5]undec-8-en-1-one in 70% yield after chromatography (pentane/ether 98/2) and in the form of a mixture of 3 isomers in the following ratio: 3/4.5/2.

MS (main isomer) : 222(M+, 43) ; 153(23), 140(45), 109(75), 95(82), 81(59), 67(55), 55(68), 41(100).

¹H-NMR : 0.64-0.70 (m, 3H), 0.81-0.88 (m, 3H), 1.03-1.13 (m, 6H), 1.18-1.82 (m, 13H), 2.09-2.49 (m, 1H).

5

2,2,7,11-tetramethylspiro[5.5]undecan-1-one

Was obtained from 2,2,7,11-tetramethylspiro[5.5]undec-8-en-1-one in 83% yield after chromatography (pentane/ether 98/2) and in the form of a mixture of 2 isomers in the following ratio: 7/1.

10 MS (main isomer) : 222(M+, 30) ; 153(38), 109(100), 95(57), 81(39), 69(39), 55(43), 41(57).

¹H-NMR MS (main isomer) : 0.64 (d : J = 7, 3H), 0.81 (d : J = 7, 3H), 1.05 (s, 3H), 1.10 (s, 3H), 1.29-1.93 (m, 11H), 2.03 (s, 1H), 2.16 (s, 1H), 2.35 (s, 1H).

15 *3. General procedure for the reduction of spiroketones with LiAlH₄*

A solution of spiro-ketone (145.6 mmol) in THF (150 ml) was added to a cold (0° C) slurry of LiAlH₄ (5.7 g, 150 mmol) in THF (600 ml). The reaction was warmed up to room temperature, and then heated at 50° C for 4 hours. After cooling to 0° C, were successively and cautiously added water (6 ml), 5 % aqueous NaOH (17 ml) and again
20 water (6 ml). The reaction was stirred at room temperature until it became a white slurry which was dried by adding anhydrous Na₂SO₄. Filtration and evaporation of solvents was followed by bulb-to-bulb distillation.

2,2,11-trimethylspiro[5.5]undec-8-en-1-ol

25 Was obtained from 2,2,11-trimethylspiro[5.5]undec-8-en-1-one in 94% yield and in the form of a mixture of 3 isomers in the following ratio: 7/1/1.

MS (main isomer) : 208(M+, 22) ; 190(40), 105(80), 93(100), 79(38), 69(19), 55(21), 41(17).

¹H-NMR (main isomer) : 0.87 (d : J = 7, 3H), 1.03 (s, 6H), 1.12-1.53 (m, 7H), 1.71 (m, 1H), 1.90 (m, 1H), 2.10(m, 1H), 2.25 (m, 1H), 3.29 (d : J = 4, 1H ; become s by
30 addition of D₂O), 5.68 (m, 2H).

2,2,9,11-tetramethylspiro[5.5]undec-8-en-1-ol

Was obtained from 2,2,9,11-tetramethylspiro[5.5]undec-8-en-1-one in 74% yield and in the form of a mixture of 2 isomers in the following ratio: 2.3/1. The two isomers may be separated by GC on a Carbowax column, 30m x 0.25mm, at 120°-240°C.

5 MS (1st eluted peak) : 222(M+, 12) ; 204(32), 119(72) , 107(100), 93(31), 79(21), 67(28), 55(40), 41(59).

MS (2nd eluted peak) : 222 (M+, 3) ; 204(12), 119(35), 107(100), 91(23), 79(14), 67(16), 55(27), 41(38).

10 ¹H-NMR : 0.80-0.86 (m, 3H), 0.97-1.05 (m, 6H), 1.07-1.24 (m, 3H), 1.11-1.60 (m, 5H), 1.64 (s large, 3H), 1.80-2.06 (m, 2H), 2.16-2.32 (m, 1H), 6.61 (m, 1H), 3.25 (d : J = 4, 1h, become s by addition of D₂O), 5.38 (m, 1H).

2,2,7-trimethylspiro[5.5]undecan-1-ol

15 Was obtained from 2,2,7-trimethylspiro[5.5]undecan-1-one in 85% yield after chromatography (on SiO₂, eluent: pentane/ether = 9/1) and in the form of a mixture of 2 isomers in the following ratio: 1/1 mixture. The two isomers may be separated by GC on a SPB-1 column, 30m x 0.25mm, at 120°-240°C.

MS (1st eluted peak) : 210 (M+, 85) ; 122(52), 109(65), 96(78), 82(100), 67(40), 55(45), 41(29).

20 MS (2nd eluted peak) : 210 (M+, 60) ; 122(62), 109(81), 96(86), 82(100), 67(48), 55(55), 41(35).

¹H-NMR : 0.82 and 0.89 (d : J = 7, 3H) ; 0.93, 0.98, 1.02 and 1.07 (s, 6H) ; 1.10-2.22 (m, 15H), 3.30 and 3.63 (d : J = 6, become s by addition of D₂O, 1H).

25 *2,2,7,11-tetramethylspiro[5.5]undecan-1-ol*

Was obtained from 2,2,7,11-tetramethylspiro[5.5]undecan-1-one in quantitative yield and in the form of a mixture of 3 isomers in the following ratio: 1/16/2.

Organoleptic properties: a natural woody odor with connotation of the cedar, atlas cedar type together with terpenes bottom notes.

30 MS (main isomer) : 224 (M+, 48) ; 123(23), 109 (100), 95(58) , 82(40), 69(28), 55(29), 41(20).

¹H-NMR (main isomer) : 0.83 (d : J = 7, 3H), 0.97 (s, 3H), 1.06 (s, 3H), 1.22 (d : J = 7, 3H), 1.10-1.93 (m, 13H), 2.17 (m, 1H), 2.35 (m, 1H), 3.37 (d : J = 5, become s by addition of D₂O, 1H).

5 4. General procedure for the esterification of alcohols

To a solution of the spiro-alcohol (1 equivalent) in pyridine (1000% in weight) was added acetic anhydride (10equivalents) and the mixture was heated at 115° until completion of the reaction (GC). After cooling, the residue was extracted with ether, washed successively with water, 10% aqueous HCl, saturated NaHCO₃, brine, dried over Na₂SO₄,
10 and concentrated under vacuum. The crude acetates were purified by flash chromatography (on SiO₂, eluent: pentane/ether = 95/5) and by bulb to bulb distillation.

2,2,11-trimethylspiro[5.5]undec-8-en-1-yl acetate

Was obtained from 2,2,11-trimethylspiro[5.5]undec-8-en-1-ol in 58% yield and in the
15 form of a mixture of 3 isomers in the following ratio: 7/1/1.

Organoleptic properties: an odor of the woody, amber/ambergris and cedar type.

MS (main isomer) : 250 (M⁺, 0) ; 190(99), 105(100), 93(66), 79(31), 69(16), 55(18),
43(37).

¹H-NMR (main isomer) : 0.86 (d : J = 7, 3H), 0.96 (s, 6H), 1.15-1.70 (m, 8H), 1.82 (m,
20 1H), 2.20 (s, 3H), 2.18 (m, 1H), 2.53 (m, 1H), 4.78 (s, 1H), 5.50 (m, 1H), 5.58 (m, 1H).

2,2,9,11-tetramethylspiro[5.5]undec-8-en-1-yl acetate

Was obtained from 2,2,9,11-tetramethylspiro[5.5]undec-8-en-1-ol in quantitative yield
25 and in the form of a mixture of 2 isomers in the following ratio: 2.3/1.

MS (minor isomer): 264 (M⁺, 0), 204(47), 119(80), 107(79), 91(34), 79(21), 67(21),
55(35), 43(100).

MS (major isomer): 264 (M⁺, 0), 204(46), 119(100), 107(49), 91(23), 79(19), 67(19),
55(27), 43(86).

¹H-NMR : 0.79-0.86 (m, 3H), 0.94(s, 3H), 0.98 (s, 3H), 1.17-1.86 (m, 8H), 1.63 (s large, 3H), 1.98 and 1.99 (s, 3H), 2.04-2.17 (m, 2H), 2.48 (m, 1H), 4.72 and 4.75 (s, 1H), 5.19 and 5.29 (m, 1H).

5 5. Procedure for the etherification of a spiroalcohol

7-methoxy-3,5,8,8-tetramethylspiro[5.5]undec-2-ene

To a mixture of 0.36g (2.7mmole) of KH 30% in oil and 4ml of dry THF at room temperature was added a solution of 0.5g (2.25mmole) of 2,2,9,11-tetramethylspiro[5.5]undec-8-en-1-ol in 2ml of dry THF. After 45 minutes at 25°, 0.96g (6.67mmole) of CH₃I were added, the mixture was stirred for 1hour at 25°, poured into ice, extracted with ether, washed with brine, dried on Na₂SO₄ and concentrated under vacuum. The crude product was purified by bulb to bulb distillation to give 0.55g (99%) of pure spiro-ether and in the form of a mixture of 2 isomers in the following ratio: 2.3/1.

Organoleptic properties: a nice woody odour with vetyver, aromatic and labdanum notes.

15 MS (major isomer): 236 (M+, 11), 204 (46), 119(85), 107(100), 93(41), 79(26), 67(24), 55(38), 41(58).

MS (minor isomer): 236(M+, 6, 204(30), 119(40), 107(100), 91(28), 79(18), 67(15), 55(26), 41(37).

¹H-NMR : 0.78-0.85 (m, 3H), 0.98 and 0.99 (s, 6H), 1.04-2.26 (m, 13H), 2.52 (m, 1H), 2.74 (m, 1H), 3.44 and 3.46 (s, 3H), 5.26 and 5.32 (m, 1H).

Example 3

Preparation of a perfuming composition

25

A composition of the "floral-violet" type was prepared by admixing the following ingredients:

<u>Ingredient</u>	<u>Parts by weight</u>
30 Hexylcinnamic aldehyde	150
Cetalox ^{® 1)}	20
2-pentyl-1-cyclopentol ²⁾	30

	10%* Farenal ³⁾	50
	Florol ^{® 4)}	100
	Hedione ^{® 5)}	150
	Linalool	200
5	Mayol ^{® 6)}	100
	Myrrh essential oil	15
	10%* Rose oxide	40
	Red thyme essential oil	25
	Parmanthene ⁷⁾	<u>20</u>
10		900

* in dipropyleneglycol

- 1) 8,12-epoxy-13,14,15,16-tetranorlabdane; origin : Firmenich SA, Geneva, Switzerland
- 2) origin : Firmenich SA, Geneva, Switzerland
- 3) origin : Haarmann & Reimer
- 15 4) tetrahydro-2-isobutyl-4-methyl-4(2H)-pyranol; origin : Firmenich SA, Geneva, Switzerland
- 5) methyl dihydrojasmonate ; origin : Firmenich SA, Geneva, Switzerland
- 6) cis-7-P-menthanol; origin : Firmenich SA, Geneva, Switzerland
- 7) compounded perfumery base; origin : Firmenich SA, Geneva, Switzerland

20

The addition of 100 parts by weight of 2,2,9,11-tetramethylspiro[5.5]undec-8-en-1-yl acetate imparted to the hereinabove-mentioned "floral-violet" composition a very nice and powerful amber/ambergris connotation and transformed the starting composition in a more complex et powerful accord.

25

Example 4

Preparation of a perfuming composition

- 30 A composition of the "woody-amber" type was prepared by admixing the following ingredients:

	<u>Ingredient</u>	<u>Parts by weight</u>
	Benzyl acetate	70
	Eugenol	60
	Florol ^{® 1)}	100
5	Hedione ^{® 2)}	60
	Irاليا ^{® total 3)}	180
	Phenethylol	150
	Benzyl salicylate	300
	Wardia ^{® 4)}	<u>50</u>
10		970

* in dipropylene glycol

- 1) tetrahydro-2-isobutyl-4-methyl-4(2H)-pyranol; origin : Firmenich SA, Geneva, Switzerland
- 2) methyl dihydrojasmonate ; origin : Firmenich SA, Geneva, Switzerland
- 15 3) mixture of methyl-ionone; origin : Firmenich SA, Geneva, Switzerland
- 4) compounded perfumery base; origin : Firmenich SA, Geneva, Switzerland

The addition of 30 parts by weight of 2,2,9,11-tetramethylspiro[5.5]undec-8-en-1-yl acetate is sufficient to impart to the hereinabove-mentioned simple composition for functional perfumery a very perceivable amber/ambergris connotation and increased the functional aspect of the above-mentioned composition.

Example 5

25 Preparation of a perfuming composition

A man perfume base composition of the "woody-citrus" type was prepared by admixing the following ingredients:

30	<u>Ingredient</u>	<u>Parts by weight</u>
	Linalyl acetate	400
	Bergamot essential oil	200

	Cedramber	400
	Citral	20
	Citronellol	80
	4-cyclohexyl-2-methyl-2-butanol ¹⁾	150
5	Coumarin	80
	Geranium essential oil	30
	Hedione [®] HC ²⁾	200
	Lavandin	200
	Lyrat [®] ³⁾	250
10	50%* Oakmoss	40
	Patchouli	400
	Polysantol [®] ⁴⁾	50
	Clary-sage essential oil	40
	Vanilline	20
15	Vertofix coeur ³⁾	400
	Tamarine Base 41310 ⁴⁾	40
		<u>40</u>
		3000

* in dipropyleneglycol

- 20 1) origin : Firmenich SA, Geneva, Switzerland
 2) methyl dihydrojasmonate ; origin : Firmenich SA, Geneva, Switzerland
 3) origin : International Flavors & Fragrances, USA
 4) 3,3-dimethyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-4-penten-2-ol; origin :
 Firmenich SA, Geneva, Switzerland
 25 5) compounded perfumery base; origin : Firmenich SA, Geneva, Switzerland

The addition of 300 parts by weight of 2,2,11-trimethylspiro[5.5]undec-8-en-1-ol to the hereinabove-mentioned composition boosted, exalted the patchouli note. If, instead of adding the invention compound, where added the same amount of patchouli the overall
 30 fragrance would have been less woody, rich and rooty and with a much less pronounced volume, loosing therefore in performance and quality.

Example 6Preparation of a perfuming composition

- 5 A man perfume base composition of the "citrus-herbaceous-spicy" type was prepared by admixing the following ingredients :

	<u>Ingredient</u>	<u>Parts by weight</u>
	Geranyl acetate	20
10	Linalyl acetate	400
	10%* 4-(4-hydroxy-1-phenyl)-2-butanone	10
	Bergamot essential oil	200
	Cedroxide ^{® 1)}	200
	Citral	30
15	Sfuma Lemon essential oil	450
	4-cyclohexyl-2-methyl-2-butanol ²⁾	90
	10%* Galbanum essential oil	70
	Clove essential oil	90
	Habanolide ^{® 3)}	100
20	Hedione [®] HC ⁴⁾	30
	Helvetolide ^{® 5)}	50
	Lavander essential oil	200
	Lylal ^{® 6)}	300
	Crystal moss	20
25	Nutmeg essential oil	150
	Polysantol ^{® 7)}	60
	Cis-3-hexenol salicylate	30
	Vertofix coeur ⁶⁾	700
	Ylang Extra	<u>100</u>
30		3300

* in dipropyleneglycol

- 1) trimethyl-13-oxabicyclo-[10.1.0]-trideca-4,8-diene; origin : Firmenich SA, Geneva, Switzerland
- 2) origin : Firmenich SA, Geneva, Switzerland
- 5 3) pentadecenolide; origin : Firmenich SA, Geneva, Switzerland
- 4) methyl dihydrojasmonate ; origin : Firmenich SA, Geneva, Switzerland
- 5) (+)-(1S,1'R)-2-[1-(3',3'-dimethyl-1'-cyclohexyl)ethoxy]-2-methylpropyl propanoate; origin : Firmenich SA, Geneva, Switzerland
- 6) origin : International Flavors & Fragrances, USA
- 10 7) 3,3-dimethyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-4-penten-2-ol; origin : Firmenich SA, Geneva, Switzerland

The addition of 100 parts by weight of a mixture of 2,2,7,9-tetramethylspiro[5.5]undec-8-en-1-one and its regio isomer 2,2,8,10- tetramethylspiro[5.5]undec-8-en-1-one imparted to
15 the hereinabove-mentioned masculine composition a nice thuyonic and fruity connotation which is in-between Eucalyptus or noble laurel naturals oils. However, said connotation was more substantive and long lasting, especially in the bottom notes, than the similar connotations which could have been imparted by the addition of the above-mentioned naturals oils.

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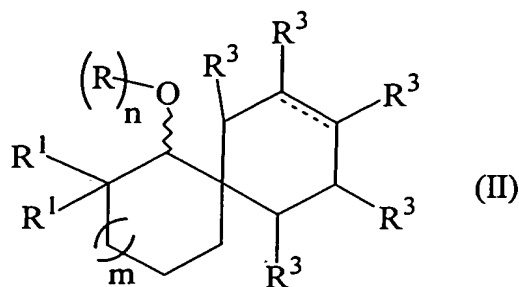


15

the wavy line represents a single bond, in which case the index n represents 1; and the dotted line represents a single or double bond;

20

2. A perfuming composition or perfumed article according to claim 1, characterized in that the perfuming ingredient is a compound of formula

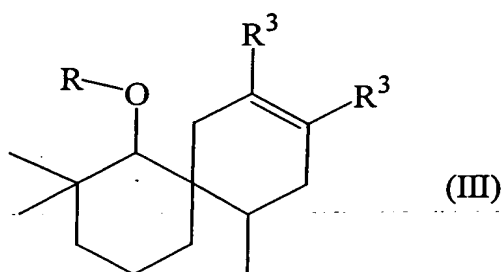


wherein the indexes m and n and the dotted and wavy lines have the same meaning as in claim 1;

5 the symbol R represents a hydrogen atom, or an acetyl group;
the symbols R¹ and R³ represent a hydrogen atom or a methyl group; and two, three or four symbols amongst R¹ and R³ represent simultaneously a methyl group ; and one, two or three of the R³ symbols, preferably non adjacent, represent simultaneously a methyl group.

10 in the form of any one of its optical or regio isomers or of a mixture thereof.

3. A perfuming composition or perfumed article according to claim 1, characterized in that the perfuming ingredient is a compound of formula



15

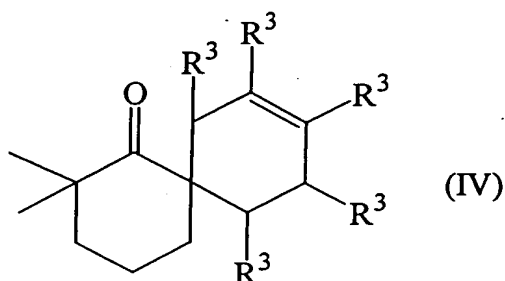
wherein the symbol R represents a hydrogen atom or an acetyl group; and
the symbols R³ represent, simultaneously, a hydrogen atom or
one symbol R³ represents a methyl group and the other symbol R³ represents a
20 hydrogen atom,

in the form of any one of its optical or regio isomers or of a mixture thereof.

4. A perfuming composition or perfumed article according to claim 2 or 3, characterized in that the perfuming ingredient is 2,2,9,11-tetramethylspiro[5.5]undec-8-

en-1-yl acetate, 2,2,11-trimethylspiro[5.5]undec-8-en-1-ol or 2,2,11-trimethylspiro[5.5]undecan-1-ol.

5 5. A perfuming composition or perfumed article according to claim 1, characterized in that the perfuming ingredient is a compound of formula



10 wherein two symbols R^3 represent a methyl group and the other symbols R^3 represent a hydrogen atom,
in the form of any one of its optical or regio isomers or of a mixture thereof.

15 6. A perfuming composition or perfumed article according to claim 2 or 5, characterized in that the perfuming ingredient is a mixture of 2,2,7,9-tetramethylspiro[5.5]undec-8-en-1-one and 2,2,8,10-tetramethylspiro[5.5]undec-8-en-1-one, a mixture of 2,2,10-trimethylspiro[5.5]undec-8-en-1-one and 2,2,7-trimethylspiro[5.5]undec-8-en-1-one or 2,2-dimethylspiro[5.5]undec-8-en-1-one.

20 7. A perfuming composition or perfumed article according to any one of claims 1 to 6, in the form of a perfume, cologne or after-shave lotion, a perfumed soap, a bath salt, mousse, oil or gel preparation for the shower or the bath, a shampoo, a body deodorant or antiperspirant, a body oil or body-care product, an ambient air deodorant, a liquid or solid detergent for textile treatment, a detergent composition or a cleaning product for dishes or varied surfaces, a fabric softener or a cosmetic preparation.

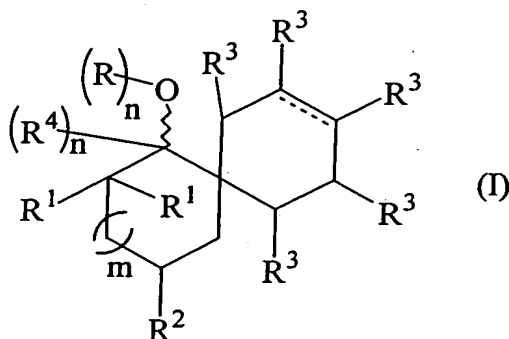
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8. Use as perfuming ingredient of a compound as defined in any one of claims 1 to 6.

9. A compound of formula as defined in any one of claims 1 to 6, provided that 2,8-dimethyl spiro[5,5]undec-8-en-1-one, 2,9-dimethyl spiro[5,5]undec-8-en-1-one, 1,9-dimethyl spiro[5,5]undec-8-en-1-ol, 1,8-dimethyl spiro[5,5]undec-8-en-1-one, 8,9-dimethyl spiro[5,5]undec-8-en-1-one and 7,8-dimethyl spiro[4,5]dec-7-en-1-one are
5 excluded.

Abstract

The present invention relates to the perfumery industry. It concerns more particularly a compound of formula (I)



wherein the index m is 0 or 1; the symbol R represents a hydrogen atom, or a methyl or acetyl group; the symbols R^1 , R^2 and R^4 represent a hydrogen atom or a methyl group; the symbol R^3 represents a hydrogen atom, or a methyl or ethyl group; and two, three or four symbols amongst R^1 to R^4 represent simultaneously a group containing at least a carbon atom; and the wavy and dotted lines represent a double bond, in which case n represents 0; or the wavy line represents a single bond, in which case the index n represents 1; and the dotted line represents a single or double bond.

The invention also relates to the use of the invention compounds as perfuming ingredients, able to impart a woody and/or aromatic, as well as to the perfumed articles or perfuming compositions comprising as active ingredient a compound of formula (I).